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Southern Research Inst, Birmingham, AL

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RESIDUAL MONOMERS IN ACRYLIC AND MODACRYLIC FIBERS AND FABRICS

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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The report deals with the detection and quantitation of acrylonitrile, vinylidene chloride, and vinyl bromide, which are used as monomers in the production of acrylic and modacrylic fibers. The amounts of monomers evolved from samples of carpets, fibers, and fabrics at 50 °C and 50% relative humidity were determined by gas chromatography with a flame ionization detector and by direct insertion probe mass spectroscopy. The results of the gas chromatographic studies indicate that detectable amounts of residual acrylonitrile, vinylidene chloride, and vinyl bromide were not released from the carpet, fiber, and fiber samples under the conditions selected for analysis. Direct insertion mass spectrometry indicated that methyl bromide was evolved from all of the fiber samples and from two of the three carpet samples. From the remaining carpet sample, three halogenated compounds—dibromodichloroethanol, tetrabromoethanol, and tribromochloroethanol—were identified. Traces of fatty acids were found in all of the samples, and sulfur dioxide was evolved from all of the samples except the fabric sample.

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PREFACE

This report describes a study conducted under Task Order No. 3 of the U.S. Environmental Protection Agency Contract No. 68-01-4746. This effort was part of an overall service performed under task requests to generate analytical data on a specified chemical, a group of chemicals, or commercial products by conducting specific tests, analyses, or experiments within several broad areas of interest.

TABLE OF CONTENTS

		Page
SECTION 1	INTRODUCTION	1
SECTION 2	CONCLUSIONS	2
SECTION 3	RECOMMENDATIONS	3
SECTION 4	EXPERIMENTAL PROCEDURES	4
	EVOLUTION APPARATUS	4
	EVOLUTION, ADSORPTION, AND DESORPTION OF MONOMERS	4
	GAS CHROMATOGRAPHIC ANALYSIS	6
	DIRECT INSERTION MASS SPECTRAL ANALYSIS . .	7
SECTION 5	EXPERIMENTAL RESULTS	8
EPA Form 2220-1	. . . . .	10

SECTION 1

INTRODUCTION

This report deals with the detection and quantitation of acrylonitrile, vinylidene chloride, and vinyl bromide, which are used as monomers in the production of acrylic and modacrylic fibers. These three monomers were selected for study because of concern over their adverse health effects (e.g., their potential carcinogenicity).

The task order for the analytical work described in this report called for the detection and quantitation of specific residual monomers in six samples of materials furnished by the Environmental Protection Agency. The samples were labeled Blue Carpet, Yellow Carpet, Brown Carpet, Fiber A, Fiber M, and Blue Fabric. The samples representing three types of products—carpets, fibers and fabrics—were analyzed for acrylonitrile, vinylidene chloride, and vinyl bromide by gas chromatography with a flame ionization detector and by direct insertion probe mass spectrometry.

SECTION 2

CONCLUSIONS

The results of the gas chromatographic studies indicate that detectable amounts of residual acrylonitrile, vinylidene chloride, and vinyl bromide are not released from the carpet, fiber, and fabric samples under the conditions selected for analysis. On the other hand, analysis of the six samples by direct insertion mass spectrometry indicate that methyl bromide is evolved from the Yellow Carpet, Brown Carpet, Fiber A, and Fiber M. Three halogenated compounds—dibromodichloroethanol, tetrabromoethanol, and tribromochloroethanol—were identified from one sample, Blue Fabric. Traces of fatty acids were found in all of the samples, and sulfur dioxide was found in all of the samples except the Blue Fabric.

SECTION 3

RECOMMENDATIONS

Because of the potential toxicity of methyl bromide, additional studies are recommended to quantify the amounts that were identified in some of the samples. Methyl bromide is a potent fumigant gas, and it is one of the most toxic of the common alkyl halides.[1] Death following acute poisoning is usually caused by the irritating effect of methyl bromide on the lungs. In chronic poisoning, death is due to the toxic effect of methyl bromide on the central nervous system. Fatal poisoning in man has always resulted from exposures to relatively high concentrations of methyl bromide vapors (8,600 to 60,000 ppm), whereas nonfatal poisoning has resulted from exposure to concentrations as low as 100 to 500 ppm. Locally, methyl bromide is an extreme irritant to the skin.

In future work, an analytical procedure for the detection and quantitation of methyl bromide could be based on Sampling and Analysis Method No. S-372 developed by the National Institute for Occupational Safety and Health.[2] In this procedure, the evolved gas is sorbed on charcoal, desorbed with carbon disulfide, and analyzed by gas chromatography.

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[1]Sax, N. I. Dangerous Properties of Industrial Materials. 5th ed. Van Nostrand Reinhold Co., New York, 1979 p. 810.

[2]NIOSH Manual of Analytical Methods, Vol. 3, Part II, 2nd ed. National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1977. Method Number S-372.

SECTION 4

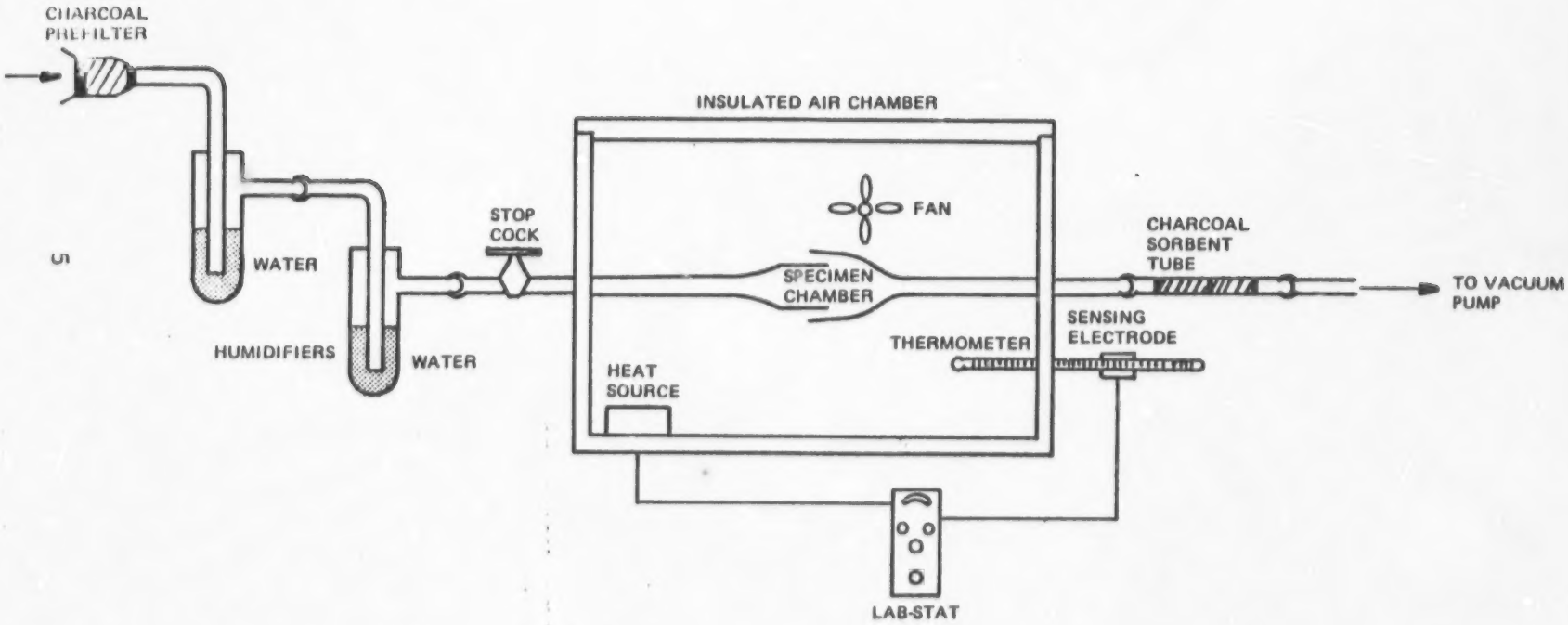
EXPERIMENTAL PROCEDURES

EVOLUTION APPARATUS

The apparatus that was constructed to simulate environmental conditions for the collection of residual monomers evolved from the carpet, fiber, and fabric samples is illustrated in the figure on page 5. The insulated air chamber was a Styrofoam ice chest containing a light bulb as a heat source and a paddle-blade fan to circulate the warmed air through the chamber. Temperature was controlled by a Matheson Labstat. The specimen chamber was connected to a charcoal prefilter and a humidifier at the inlet side, and a charcoal sorbent tube was located at the outlet side for collection of monomer vapor. The chamber temperature was maintained at 50 °C, and the relative humidity of the air within the chamber was 50%. Air was drawn through the chamber and through the sorbent tube at 1.2 L/min. The conditions within the chamber were selected because they probably represent the most adverse conditions that carpets, fibers, and fabrics may be exposed to in their natural environment.

EVOLUTION, ADSORPTION, AND DESORPTION OF MONOMERS

Weighed portions of the samples furnished by EPA were equilibrated for 30 min at 50 °C in the all-glass specimen chamber. Subsequently, moistened air was swept through the speci-



Schematic Diagram of the Monomer Evolution Apparatus

men chamber and then the sorbent tube. The evolved gases were adsorbed on chromotographic grade, activated charcoal (Applied Science Laboratories, Inc., State College, Pa.) packed in the sorbent tube. After collection of the sample, the adsorbed volatiles were extracted from the charcoal with 1 mL of methanol, and aliquots of the extract were analyzed for acrylonitrile, vinylidene chloride, and vinyl bromide by gas chromotography.

GAS CHROMATOGRAPHIC ANALYSIS

The gas chromatographic analyses were performed with a Perkin-Elmer Model 910 gas chromatograph equipped with a flame ionization detector. Separation of the monomers was performed on a 1.8 m x 2 mm (i.d.) glass column packed with Chromosorb 101. A temperature program was used in which the initial temperature was maintained for 4 min at 75 °C, then increased at 5 °C per min to a final temperature of 120 °C, and held at 120 °C for 2 min. Injector and detector temperatures were both 120 °C. Nitrogen was used as the carrier gas at a flow rate of 20 mL/min. Under these conditions, the limits of detection for acrylonitrile, vinylidene chloride, and vinyl bromide were typically 1, 2, and 2 ng, respectively, at a signal-to-noise ratio of 2 to 1. As explained on page 8 of this report, the limits of detection are equivalent to 0.02 and 0.04 ppm of monomer in a 10-g sample of polymer.

The gas chromatograph was calibrated by injecting standard solutions of acrylonitrile, vinylidene chloride, and vinyl bromide. The following retention times were typical: acryloni-

trile, 12.4 min; vinylidene chloride, 11.4 min; and vinyl bromide, 8.8 min.

DIRECT INSERTION MASS SPECTRAL ANALYSIS

Mass spectral measurements were made by the direct insertion technique with a Varian MAT 311A mass spectrometer. Use of the direct insertion technique involves the introduction of a small portion of the sample, as is, into the ion source of the mass spectrometer. The technique may be used with or without temperature programming. Since many factors affect the intensities of the peaks, the technique is not strictly quantitative; however, the limit of sensitivity of the method is in the subnanogram to nanogram range. In this manner, the fibers of each sample were introduced into the mass spectrometer under a reduced pressure of about 1×10^{-6} torr. The spectra were recorded at probe temperatures ranging from 20 to 300 °C. All compounds that were identified were evolved at temperatures as low as 20 °C and the amounts evolved increased with increasing temperatures until the quantities present were depleted.

SECTION 5

EXPERIMENTAL RESULTS

Gas chromatography and direct insertion mass spectrometry indicated that acrylonitrile, vinylidene chloride, and vinyl bromide were not evolved in detectable amounts from any of the six samples of carpets, fibers, and fabric furnished by EPA. The minimum detectable amounts of the monomers were 1, 2, and 2 ng for acrylonitrile, vinylidene chloride, and vinyl bromide, respectively, by gas chromatography. These values correspond to detection limits of 0.02 or 0.04 ppm of monomer in a 10-g sample of polymer.*

Direct insertion mass spectrometry, however, did reveal the presence of methyl bromide in four of the samples: Yellow Carpet, Brown Carpet, Fiber A, and Fiber M. Also, three halogenated compounds—dibromodichloroethanol, tetrabromoethanol, and tribromochloroethanol—were identified in one sample, Blue Fabric. Traces of palmitic and stearic acids were found in all of the samples. Sulfur dioxide was also found in all of the samples except the Blue Fabric.

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*The maximum volume of methanol in which 1 or 2 ng of monomer could be detected was 5 μL. The total volume of methanol extractant was 1 mL. Thus, the minimum quantity of monomer in the methanol that could be accounted for was 0.2 or 0.4 μg, representing 0.02 or 0.04 ppm of the polymer.

All of the organic halides were observed at a probe temperature of 20 °C and, therefore, do not appear to be thermal decomposition products. The halogenated ethanols evolved from the sample may have been hydrolysis products of flame retardants. At this time, an explanation for the presence of methyl bromide, a fumigant, is not available. A possible source of the fatty acids is the esters that may have been used as spin finish agents during the manufacture of the fibers. The sulfur dioxide may have resulted from an anti-oxidant formulation.